THE MELTING AND CRYSTALLIZATION KINETICS OF
HYDROGENATED POLYBUTADIENE(U) FLORIDA STATE UNIV
TALLAHASSEE DEPT OF CHEMISTRY L MANDELKERN ET AL. 1988

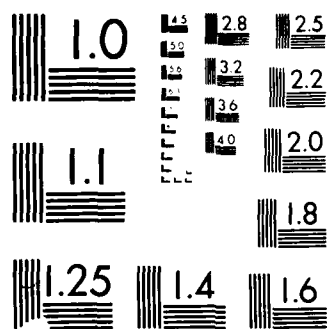UTION TEST CHART

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The Melting and Crystallization Kinetics of Hydrogenated Polybutadiene

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Introduction

The overall isothermal crystallization kinetics of a series of hydrogenated polybutadienes having narrow molecular weight and composition distributions have been studied using calorimetric and dilatometric techniques (1). In addition to the general inquiry into the crystallization kinetics and mechanisms of such well-constituted and characterized samples, the study was also promoted by the unusual melting temperatures and levels of crystallinity that are observed with molecular weight. The hydrogenated polybutadienes can be considered as copolymers with a random distribution of ethyl side groups and serve as ideal models for crystallizable random copolymers because of the narrow molecular weight and composition distribution. Special attention has been given to the influence of molecular weight and co-unit content on the crystallization process and to the long-time crystallization rate.

The characteristics of the samples studied are given in Table I. For copolymers containing 2.3 mole percent ethyl branch points the molecular weights, $M_w/M_N \leq 1.10$, ranged from 6.95×10^3 to 4.6×10^5. Carbon-13 nmr studies have shown virtually identical sequence distributions for this series of copolymers. For two other copolymers, each with $M_w = 5 \times 10^4$, the mole percent branch points were 4.14 and 5.68 respectively. The crystallization kinetic studies were carried out using conventional dilatometric techniques (2). Melting temperatures and enthalpies of fusion were determined by differential scanning calorimetry. In addition to the enthalpy of fusion measurement, the crystallinity level as well as the proportion of disordered, liquid-like and interfacial regions were determined by the analysis of the internal mode region of the Raman spectra (3)(4).

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Table I

Molecular Characteristics of Hydrogenated Polybutadienes

Designation	M_w	Mol % Ethyl Branch Points
HPBD-6950	6950	2.36
HPBD-24	24000	2.30
HPBD-49	49000	2.30
HPBD-79	79000	2.44
HPBD-460	460000	2.30
HPBD-98	50000	4.14
HPBD-97	50000	5.68

Results and Discussion

Prior to analyzing the results of the isothermal crystallization kinetics and its consequences, it is of interest and pertinent to examine some static properties. It is found, contrary to previous conclusions (5), that for rapidly crystallized (quenched) samples that the level of crystallinity is very dependent on molecular weight. For the 2.3 mole percent branch point sample the level of crystallinity decreases from 55% to 25% as the molecular weight increases. This molecular weight dependence is very similar to that observed for linear polyethylene and other homopolymers. However, the corresponding level of crystallinity of the copolymers is significantly reduced. The observed dependence of the melting temperature on molecular weight was rather surprising. After either rapid crystallization or crystallization at the borderline of isothermalicity, for samples with fixed branching content and subsequent rapid heating, the melting temperature decreases about 7°C. This result is opposite to that observed for the corresponding linear polymer and to theoretical expectations. The basis for this unexpected behavior appears to be of kinetic origin. It is one of the motivating reasons for investigating the crystallization kinetics in detail.

Certain salient features emerge from the dilatometric studies. Among these is the fact that there is a very marked dependence of both molecular weight and crystallization temperature (at the same undercooling) on the crystallization rate. Consequently very little overlap in the crystallization temperatures can be obtained between the molecular weight fractions. In order to study the kinetics in a reasonable time scale it was found that the crystallization of higher molecular weights needs to be carried out at much lower temperatures than lower molecular weights although their equilibrium melting temperatures are the same. In a general sense the crystallization kinetics follow Avrami type isotherms for the early stages of the transformation, but major modifications are observed which depend on molecular weight, chain structure and crystallization temperature. For the 2.3 mole percent copolymers of high molecular weight,

which have to be crystallized at larger undercoolings, a set of superposable isotherms is observed which is very similar to those found for homopolymers. As the molecular weight decreases, and the temperature range for crystallization increases, superposable isotherms are observed at the lower crystallization temperature for each sample. However, deviations are observed at the higher temperatures. For the higher co-unit content copolymers superposable isotherms are not observed in the accessible temperature range for isothermal crystallization.

The long-time crystallization rate, as characterized by the slope in the linear plot of the level of crystallinity against log t, is dependent on both molecular weight and crystallization temperature. For a given molecular weight the slope increases rapidly with crystallization temperature. For molecular weights above about 2×10^4 there is a strong dependence on chain length with increasing temperature. These results are quite different from those previously reported for linear polyethylene where there is only a very slight molecular weight dependence and for a given molecular weight the slope is independent of temperature. These observations set the basis for studying the long-time changes in the properties of the hydrogenated polybutadienes as well as other random crystallizing copolymers.

The level of crystallinity that can be attained under isothermal crystallization conditions is very low and depends on the molecular weight and crystallization temperature. For the 2.3 mole percent copolymer, the crystallinity levels range from 7-15% for $M = 4.6 \times 10^5$ and 3-15% for $M = 6.95 \times 10^3$ and decrease as the crystallization temperature increases. Consequently, the level of crystallinity that is observed at ambient temperature is a result of the cooling process and is sensitive to it. Increasing the branching content further reduces the level of crystallinity that can be attained isothermally. The major contribution to the crystallinity level at all molecular weights is that which forms on cooling. This in turn is reflected in the morphology and structure and thus on observed properties.

The difference in crystallization rate, and the limits on the temperature range in which crystallization can be conducted, appear to be the major reason for the large inversion in melting temperatures that was described. If slow heating rates are adopted, subsequent to the highest reasonable crystallization temperature, the decrease in melting temperature with molecular weight is substantially reduced so that the theoretical expectations are closer to being fulfilled.

References
(1) We wish to thank Dr. W.W. Graessley for his generosity in supplying us with these samples of hydrogenated polybutadienes.
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